

Double- k phase of the Dzyaloshinskii-Moriya helimagnet $\text{Ba}_2\text{CuGe}_2\text{O}_7$.

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(Dated: August 3, 2011)

Neutron diffraction is used to re-investigate the magnetic phase diagram of the non-centrosymmetric tetragonal antiferromagnet $\text{Ba}_2\text{CuGe}_2\text{O}_7$. A novel incommensurate double- k magnetic phase is detected near the commensurate-incommensurate phase transition. This phase is stable only for field closely aligned with the 4-fold symmetry axis. The results emphasize the inadequacy of existing theoretical models for this unique material, and points to additional terms in the Hamiltonian or lattice effects.

PACS numbers: 75.70.Tj 75.30.Kz 75.25.-j 25.40 75.50Ee

Dzyaloshinskii-Moriya (DM) antisymmetric exchange interactions [1, 2] and their role in incommensurate magnetic structures are once again at the forefront of condensed matter research. One reason for the renewed interest is the discovery of novel topological skyrmion phases in the DM helimagnet MnSi and related compounds [3, 4]. The other is the role that DM interactions play in certain scenarios of the multiferroic effect [5, 6]. Arguably, no material has attracted more attention simultaneously in both these contexts than the tetragonal DM helimagnet $\text{Ba}_2\text{CuGe}_2\text{O}_7$. This compound is one of the very few systems where DM helimagnetism can co-exist with weak-ferromagnetic behavior [7]. Moreover, theory suggested that it can support stable skyrmions, similar to those in MnSi [7]. $\text{Ba}_2\text{CuGe}_2\text{O}_7$ has an unusual soliton lattice structure in zero field [8], and shows a very interesting behavior in applied fields [9–11]. While the material itself does not demonstrate spontaneous electric polarization, the isostructural and magnetically commensurate $\text{Ba}_2\text{CoGe}_2\text{O}_7$ [12, 13] is, in fact, an unconventional multiferroic material [14].

The most spectacular feature of $\text{Ba}_2\text{CuGe}_2\text{O}_7$ is the commensurate-incommensurate (CI) transition that occurs in this material in applied magnetic fields [9, 11]. Despite the uniqueness and fundamental importance of this compound, and years of systematic studies, its exact nature remains unresolved. Theory predicts a continuous transition with a divergent periodicity, that maps onto the classic Frenkel-Kontorova model [15]. In obvious contradiction, experiments indicate a discontinuous reorientation of spins with a poorly defined “intermediate state”. The latter has been largely dismissed as a result of defect pinning [9, 11], phase separation associated with a spin-flop-like discontinuous transition [16] or a poor alignment of the applied field relative to the unique 4-fold axis of the tetragonal structure [17]. In the present study we show that none of these explanations apply. In fact, the “intermediate state” is a novel double- k incommensurate phase that exists *only* for magnetic fields *almost perfectly* aligned along the 4-fold axis. Being very unlike anything predicted for this material,

the double- k structure undermines all existing theoretical descriptions of $\text{Ba}_2\text{CuGe}_2\text{O}_7$.

The crystal and magnetic structures of $\text{Ba}_2\text{CuGe}_2\text{O}_7$ are reviewed in detail in Ref. 11. The magnetism is due to Cu^{2+} ions that form a square lattice, cell-centered in the (a, b) plane of the tetragonal non-centric $P4_21m$ structure (Fig. 1b in Ref. [11]). Long-range helimagnetic ordering occurs at $T_N = 3.2$ K. To a good approximation, the low-temperature spin arrangement is a cycloid with propagation vectors $(1 \pm \xi_0, \pm \xi_0, 0)$, $\xi_0 = 0.027$, and the spins rotating in the $(\pm 1, \mp 1, 0)$ planes, respectively, as illustrated in Fig. 1a of Ref. [11]. $(1, 0, 0)$ being the (π, π) point for the square lattice, nearest-neighbor spins are aligned almost antiparallel to each other. Due to tetragonal symmetry, one typically observes two equivalent magnetic domains with propagation vectors $(1 + \xi_0, \xi_0, 0)$ and $(1 + \xi_0, -\xi_0, 0)$, respectively. Field-cooling in a magnetic field as small as a few tens of Gauss applied in the (a, b) plane ensures a single-domain structure [10]. A more sizable in-plane field tends to re-orient the spin rotation plane of the entire cycloid to be perpendicular to the field direction. This is accompanied by a continuous and rather spectacular rotation of the propagation vector [10]. The above-mentioned CI transition occurs in magnetic fields applied along the c axis. It is preceded by a strong deformation of the planar cycloid, that in applied fields is better described as a “soliton lattice” [9, 11]. Beyond $H_c \sim 2.1$ T the system is a commensurate AF with propagation vector $(1, 0, 0)$. The focus of the present study is what happens *just before* this commensuration.

A weak point of all previous neutron diffraction studies was a less than perfect alignment of the magnetic field with respect to the c axis. On the one hand, this misalignment potentially alters the nature of the phase transition. On the other hand, measurements and the interpretation of the data are complicated by a continuous redistribution of intensity between the two tetragonal domains. The latter is due to the non-zero in-plane component of the applied field, and may be history-dependent due to pinning. Thus, the first step in our strategy to clarify the issue of the “intermediate state” was to per-

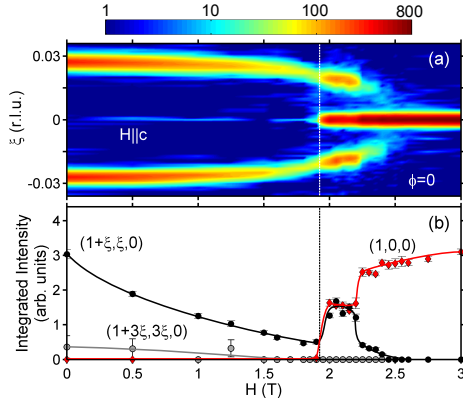


FIG. 1: (a) Neutron diffraction intensity measured in linear scans along the $(1+\xi \cos(\phi-\pi/4), \xi \sin(\phi-\pi/4), 0)$ reciprocal-space direction for $\phi = 0$ as a function of magnetic field applied along the c axis. (b) Field dependence of the integrated intensity of the incommensurate satellite reflections at ξ and 3ξ as well as of the commensurate magnetic Bragg peak at $(1,0,0)$, obtained in Gaussian fits. For the measurements of 3ξ the instrumental resolution was relaxed to optimize intensity.

form a new set of diffraction measurements in a sample with an almost perfect alignment, while diligently following a field-cooling protocol for each field value.

The data were taken on the TASP 3-axis spectrometer at Paul Scherrer Institut [18], using neutrons of incident wavevector 1.3 \AA^{-1} . The single crystal sample of mass 1.65 g was grown using the floating-zone technique and mounted in a split-coil cryomagnet. A misalignment of less than 0.5° between the nominally vertical field and the crystallographic c axis at low temperatures was achieved. The data were taken after field-cooling from 6 K to 1.6 K, in sets of elastic scans along the $(1+\xi \cos(\phi-\pi/4), \xi \sin(\phi-\pi/4), 0)$ directions in reciprocal space, for $\phi = 0$ and $\phi = \pi/2$. Here we have adopted the notation used in Ref. [10], where ϕ is the angle between the $(1,1,0)$ direction and the propagation vector. The background, primarily due to double scattering [9], was subtracted from all low-temperature scans.

The result of these measurements are summarized in Figs. 1 and 2. With increasing magnetic field, we observe a gradual change of the magnetic period ζ and a shift of intensity from the $\phi = 0$ domain to that with $\phi = \pi/2$. Even at $H = 1.7$ T a single-domain state is not achieved, though most of the intensity has shifted to $\phi = \pi/2$. This confirms an almost-perfect alignment of our sample relative to the c axis. A dramatic redistribution of intensity is seen at $H_1 = 1.9$ T. At this point the incommensurate peaks in the $\phi = \pi/2$ scans disappear. At the same time, those in $\phi = 0$ scans abruptly gain intensity. In other words, at H_1 the preferred incommensurate propagation vector abruptly rotates by $\pi/2$. Moreover, an additional peak appears in all scans in the commensurate $(1,0,0)$ position. The incommensurate peaks persist until it disappears at the CI transition at $H_c \sim 2.4$ T. We identify the field range $H_1 < H < H_c$ with the previously re-

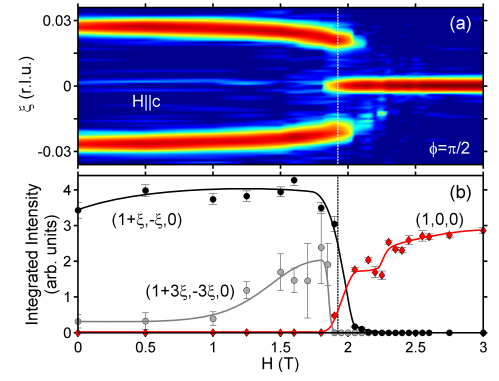


FIG. 2: Neutron diffraction data as a function of magnetic field applied along the c axis for $\phi = \pi/2$, analogous to Fig. 1. The intensity scale as given in Fig. 1 is used.

ported intermediate state.

The abrupt rotation of the incommensurate vector at H_1 suggests that this state is *not* a phase-separated mixture of the commensurate and the low-field cycloidal phases, as previously speculated, but a distinct double- k incommensurate structure. The same conclusion can be drawn from the behavior of higher-order harmonics, such as the ones at $(1+3\xi \cos(\phi-\pi/4), 3\xi \sin(\phi-\pi/4), 0)$. At $H < H_1$, the 3rd harmonic increases with field (Fig. 2 b), due to a distortion of the planar cycloid and the development of a soliton lattice [9]. In contrast, for $H_1 < H < H_c$ the harmonics are absent. The incommensurate modulation is purely sinusoidal, without distortion, and thereby distinct from that below H_1 .

A distinct incommensurate “cone” phase preceding to the CI transition was indeed predicted theoretically, for fields applied at an angle $\alpha > 0$ with respect to the 4-fold axis [17]. This phase is supposedly absent for $\alpha = 0$, and its field range progressively increases with increasing α . To verify that the observed double- k structure is not due to a residual $\alpha < 0.5^\circ$ field misalignment, we systematically investigated the behavior in canted fields.

In the first such measurement the field was applied at an angle $\alpha = 5^\circ$ relative to the c axis, in the $(1,0,0)$ plane. Despite the much larger misalignment angle, we observe an almost unchanged behavior. These data are summarized in Fig. 3 a-c. Due to a sizable in-plane field component, only one domain, with $\phi \sim 0$, survives beyond 0.5 T applied field. The same in-plane component induces a gradual rotation of the incommensurate peak around the $(1,0,0)$ position, ϕ changing from $\phi = 0$ at $H = 0$ to $\phi \sim 15^\circ$ at $H = 1.9$ T in agreement with Ref. [10]. The direction of the propagation vector was determined by centering the incommensurate peaks at each field. The ξ -scans that make up the false-color plot in Fig. 3 b are thus performed along the $(1+\xi \cos(\phi-\pi/4), \xi \sin(\phi-\pi/4), 0)$ direction with a field-dependent ϕ . As for zero tilt, at $H = H_1 \sim 1.9$ T, the propagation vector abruptly rotates by precisely 90 degrees ($\phi \rightarrow \phi + \pi/2$), and a commensurate component ap-

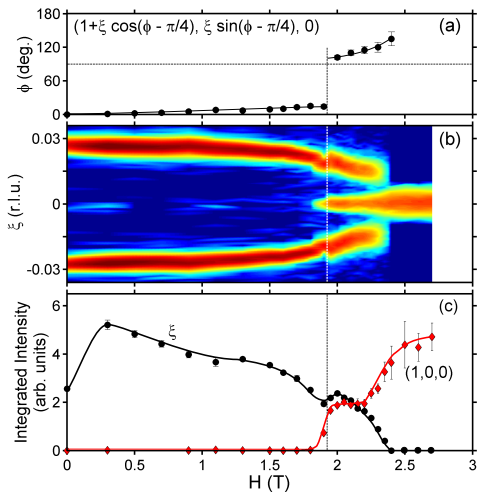


FIG. 3: Neutron diffraction data as a function of magnetic field for $\alpha = 5^\circ$. (a) Magnetic field dependence of ϕ . (b) Neutron diffraction intensity measured in linear scans along the $(1 + \xi \cos(\phi - \pi/4), \xi \sin(\phi - \pi/4), 0)$ reciprocal-space direction. The intensity scale as given in Fig. 1 is used. (c) Field dependence of the integrated intensity of the incommensurate satellite reflections at ξ as well as of the commensurate magnetic Bragg peak at $(1,0,0)$, as obtained in gaussian fits.

pears. The incommensurate peak vanishes at $H_c \sim 2.4$ T.

A key finding of this study is the double- k phase is not enhanced by a field misalignment with respect to the c axis, but is actually absent at large α angles. Data collected for $\alpha = 15^\circ$ are shown in Fig. 4. Due to a much larger in-plane field component, the propagation vector rotates more rapidly and completely aligns itself with the crystallographic $(1,0,0)$ direction: $\phi \rightarrow \pi/4$ for $H \gtrsim 1$ T. This gradual re-orientation is fully consistent with previous studies [10]. No abrupt re-orientation of the propagation vector is observed at any field. The behavior is continuous all the way to the CI transition at $H_c \sim 2.5$ T, with no sign of an additional phase at lower fields.

In contrast to small- α geometries, where the CI transition occurs in a sinusoidally modulated phase with no higher-order harmonics, for $\alpha = 15^\circ$ we observe a strong distortion of sinusoidal modulation. Indeed, as clearly seen in Fig. 4, the third (3ξ), as well as the previously unobserved 2nd (2ξ) harmonics, drastically increase in intensity as the CI transition is approached.

Note that in Fig. 4b, at $H > H_c$, the commensurate peak appears to be absent. This, however, is an instrumental effect. It stands to reason that in the commensurate AF phase, spins are aligned perpendicular to the field, i.e., along the $(1,0,0)$ direction. Neutrons are only scattered by spin components that are transverse to the scattering vector. As a result, the $(1,0,0)$ AF Bragg peak is extinguished by this polarization effect. Due to the restrictive geometry of a split-coil cryomagnet, measurements at equivalent wave vectors with more favorable polarizations were not feasible.

Preliminary data (not show) indicate virtually iden-

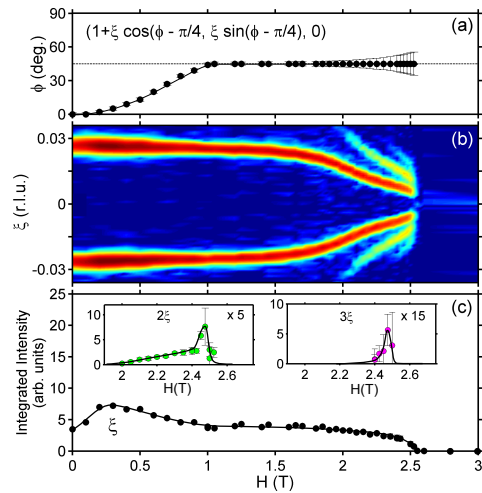


FIG. 4: Neutron diffraction data as a function of magnetic field for $\alpha = 15^\circ$, analogous to Fig. 3. The intensity scale as given in Fig. 1 is used.

tical behaviors for fields confined to the $(1,1,0)$ plane [19]. For $\alpha = 5^\circ$ the propagation vector jumps by 90° at $H_1 \sim 1.9$ T, while for $\alpha = 15^\circ$ no reorientation is observed and the peak remain at $\phi = 0$ all the way to the CI transition. We can therefore summarize all diffraction results as follows. In field applied almost parallel to the 4-fold axis, a novel sinusoidally modulated double- k phase appears just before the CI transition. When the field deviates from the high-symmetry direction, the double- k phase is absent. In this case the CI transition occurs in a complexly distorted single- k phase that continuously evolves from the zero field structure.

Even the limited diffraction data allow us to make a good guess regarding the nature of the novel double- k phase. Since it has a commensurate *antiferromagnetic* component, the double- k structure is clearly *not* the conical phase discussed in Ref. [17]. Instead, we propose that it can be approximated as an *antiferromagnetic cone* structure depicted in Fig. 5. The spins are mostly aligned in a commensurate AF pattern in the (a,b) plane. In addition, there is a small incommensurate precession of transverse spin components. We will assume that, due to tetragonal symmetry, this structure can freely rotate in the (a,b) plane, just like the soliton lattice [10]. Similarly, we can expect that the orientation of the spin rotation plane is uniquely coupled to the propagation vector.

In a field, any AF structure will always favor a spin-flop configuration. In particular, the dominant commensurate AF spin component of the proposed AF-cone structure will tend to align itself perpendicular to any in-plane component of the applied field. As a result, the spin precession plane will align *parallel* to the in-plane field component. The expected behavior for the planar soliton-lattice phase (Fig. 5b) is quite different. A small in-plane field will tend to align the spin rotation plane *perpendicular* to itself [10]. Thus the observed abrupt 90° rotation

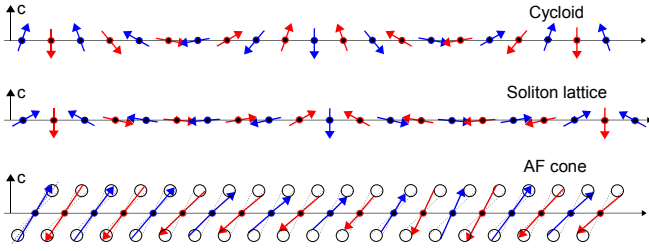


FIG. 5: Proposed magnetic structure of $\text{Ba}_2\text{CuGe}_2\text{O}_7$ for the almost AF cycloid, the soliton lattice and the AF-cone phase.

of the propagation vector at H_1 may signify a transition from the planar soliton-lattice phase at low fields to a AF-conical state at high fields.

The proposed model for the double- k structure also gives a handwaving explanation of the observed absence of higher-order harmonics. Indeed, for the planar state realized below H_1 , a distortion and formation of a soliton lattice is the only way it can respond to a field applied in the plane of spin rotation. In contrast, the AF cone state, can take advantage of the Zeeman energy by a canting of its dominant AF-commensurate component, leaving the small incommensurate modulation unperturbed.

A further understanding of the observed double- k phase will require new theoretical input. Existing models fail to predict it, and are clearly missing an important component of the physics of $\text{Ba}_2\text{CuGe}_2\text{O}_7$. The new phase appears close to the CI transition, where the soliton lattice of the original model becomes infinitely soft. Therefore, the missing terms in the Hamiltonian need not be particularly strong to qualitatively alter the energy landscape. We can suggest two potential candidates. First, many of previous theories focused only on the component of the DM vector \mathbf{D} that lies in the tetragonal (a, b) plane. Due to crystallographic symmetry, this component is uniform from one Cu-Cu bond to the next, and is responsible for all the spiral structures in $\text{Ba}_2\text{CuGe}_2\text{O}_7$. The component of \mathbf{D} that is parallel to the four-fold axis (Fig. 1b in Ref. [11]) has often been ignored. This component is sign-alternating and favors a commensurate weak-ferromagnetic canting of all spins in one direction [20]. This term is known to be dominant in the similar $\text{K}_2\text{V}_3\text{O}_8$ system [21]. If active in $\text{Ba}_2\text{CuGe}_2\text{O}_7$, it will distort any planar soliton-lattice phase, potentially giving rise to *even*-order harmonics, as those observed in this work for large α . Note that distortions due to magnetic field itself produce only odd harmonics [9]. We can speculate that this term could also play a role in stabilizing the double- k structure.

The other potential cause of the new phase is lattice effect. Indeed, all previous models were based on a continuous mapping of the original Heisenberg spin Hamiltonian. Near the CI transition though, such a description is bound to break down. In this theory, even as the distance between solitons increases near H_c , the *width* of each soliton decreases. Near the critical field it will be-

come comparable to the lattice spacing, at which point the theory will lose self-consistency.

In summary, our results show that there is more to the physics of $\text{Ba}_2\text{CuGe}_2\text{O}_7$ than previously thought. This circumstance may have a direct bearing on the stability of the predicted (but never observed) skyrmion lattice in this material [7, 20], as well as the multiferroic effect.

This work is partially supported by the Swiss National Fund through Project 6 of MANEP. We thank C. Pfleiderer, K. Conder, J. Gavilano, M. Laver, U. Rössler and A. Bogdanov for support and stimulating discussions. Technical support from M. Zolliker and M. Bartkowiak is gratefully acknowledged.

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